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Acousto-Optic and Linear Electro-Optic Properties of Organic Polymeric Materials

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<p>The potential of organic polymeric materials for use in acousto-optic and electro-optic devices operating at GHz frequencies is examined. This is accomplished by identifying and briefly discussing the important molecular properties for enhanced acousto-optic and electro-optic effects and then relating these to current polymeric materials.</p> <p style="text-align: right;">Singer ↑</p>					
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ACOUSTO-OPTIC AND LINEAR ELECTRO-OPTIC PROPERTIES OF ORGANIC POLYMERIC MATERIALS

INTRODUCTION

Currently, most acousto-optic and electro-optic devices make use of inorganic crystals as their active medium.¹⁻⁶ This is due, in part, to the historical development of device concepts and the ease in theoretically modeling such effects in crystalline versus amorphous or polycrystalline materials. Although inorganic crystals are good acousto-optic and electro-optic device materials, the search for better materials continues. It is in this spirit that we assess the use of organic polymeric materials in such devices operating in the GHz frequency range. The assessment is accomplished by identifying and briefly discussing the important molecular properties for enhanced acousto-optic and electro-optic effects and then relating these to current polymeric materials.

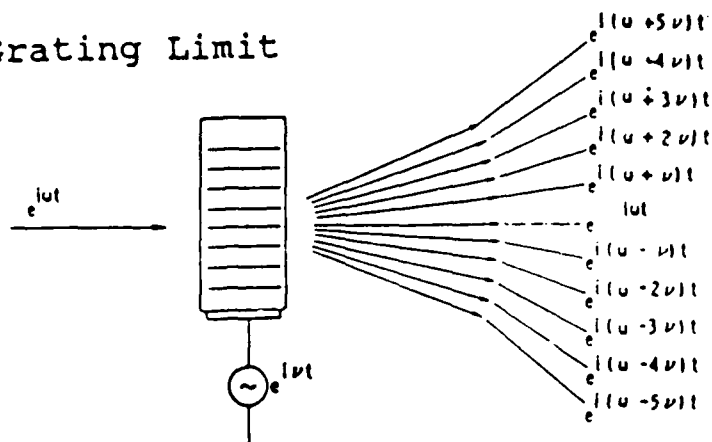
ACOUSTO-OPTIC MATERIALS AND DEVICES

Acousto-optic devices are based on changes in the optical properties of materials due to traveling pressure disturbances (acoustic waves) which produce regions of compression and rarefaction in the material. Such density disturbances cause modifications of the refractive index of the material and thereby, cause the medium to respond as a phase grating. In the thin grating limit,^{4,5,7} described by

$$\frac{2\pi\lambda L}{\Lambda^2} \ll 1 \quad (1)$$

where λ is the light wavelength, Λ is the acoustic wavelength and L is the width of the interaction region, diffraction in many orders will occur with the probe light at normal incidence.^{4,5,7} However, at large values of L , the higher order diffractions interfere with each other, completely destroying the diffraction pattern. To achieve constructive interference in a thick grating, the light beam must be set at the angle $\theta_B = \sin^{-1} \lambda/2\Lambda$.^{4,5,7} The diffracted beam will be seen at this same angle as indicated in Fig. 1. Note that there are not any

(a) Thin Grating Limit



(b) Thick Grating Limit

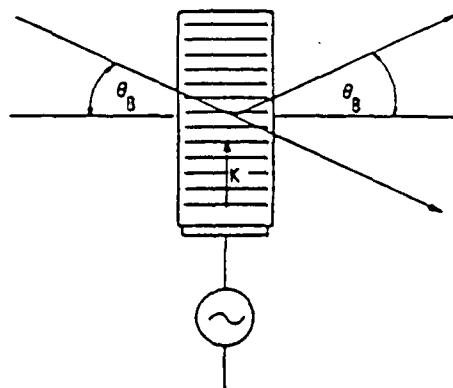


Figure 1: Schematic diagrams of the two limiting cases of diffraction from an acoustically generated phase grating. In (a) the thin limit grating is diagrammed detailing the diffracted waves' respective phases; ω is the frequency of the light and ν is the acoustic frequency. In (b) the thick limit grating is diagrammed showing the Bragg diffraction angle, θ_B . This figure is adapted from Ref. 5.

higher-order diffracted beams. (This is commonly referred to as Bragg diffraction due to its similarity to x-ray scattering from atoms in crystals.)

Several figures of merit for Bragg diffracting acousto-optic devices have been derived for use in comparing potential materials and are given below: n is the refractive index; p is the material's maximum photoelastic coefficient, the parameter of principle interest in device design; ρ is the density; and v is the acoustic velocity of the material.^{3-5,8,9}

$$M_1 = (n^7 p^2 / \rho v) \quad (2)$$

$$M_2 = (n^6 p^2 / \rho v^3) \quad (3)$$

$$M_3 = (n^7 p^2 / \rho v^2) \quad (4)$$

M_2 is an experimentally measurable quantity which gives information on the diffraction efficiency.^{3,4,8,9} The other figures of merit, M_1 and M_3 , involve considerations of the bandwidth due to the shift in the Bragg angle with acoustic frequency changes and the capacity (number of separable positions) of the material due to the size of the interaction region, respectively.^{3,4,8,9} In general, it can be seen that the most important material properties for large acousto-optic effects are a high refractive index and photoelastic constant and a low acoustic velocity.

There are two additional properties that must be considered in evaluating materials for acousto-optic applications: optical and acoustic attenuation. Attenuation refers to both absorption and scattering losses. Acousto-optic materials must have simultaneously, reduced scattering and absorption of both optic and acoustic waves.

ORGANIC MATERIALS

While data on indices of refraction and density of polymeric materials abound, data on photoelastic coefficients, acoustic velocity and acoustic attenuation in the GHz regime are very limited. Therefore, the evaluation of many polymeric materials for GHz acousto-optic applications will depend on deriving appropriate theoretical values for these parameters. Such values will be based, whenever possible, on extrapolations of lower frequency data. For the discussions that follow, it will also be assumed that the materials of interest are isotropic.

Photoelastic Coefficients

Photoelastic coefficients (P_{ijkl}) relate the strain tensor (S_{kl}) to the indicatrix ($[1/n^2]_{ij}$) where n is the index of

refraction.³⁻⁵ That is, they describe the coupling of mechanical strain to a material's optical properties.

$$\Delta(1/n^2)_{ij} = \sum_{k,l=1}^3 P_{ijkl} S_{kl} \quad (5)$$

The tensor notation is required because of the directional dependence of material properties. For an isotropic material there are only two independent photoelastic coefficients. They are related to the material properties along (longitudinal) and perpendicular (transverse) to the direction of propagation of the acoustic wave. The longitudinal photoelastic coefficient is the one of interest in device design; it is much larger than that in the transverse direction and, therefore, is the only one discussed in the sections that follow.^{3-6,8,9}

Determination of material photoelastic coefficients is still essentially an empirical science and unfortunately, very few polymeric material photoelastic coefficients have been reported (see Table 1).^{4,5} The photoelastic constants of inorganic crystals and glasses have been extensively investigated and, in general, vary between 0.2 and 0.6.^{2-6,8-10} The latter is the theoretical value of the photoelastic constant for an ideal material with a refractive index of 1.5,^{4,5} the refractive index value for nearly all carbon based polymeric materials.¹¹

Theoretical discussions of the photoelastic effect often cite Mueller's microscopic description.¹² This theory suggests that photoelastic effects arise from refractive index changes related to alterations in the material density and polarizability under strain. For most solids, a decrease in polarizability occurs when the material is compressed because of the increased orbital overlap and subsequent localization of the optical electrons. However, interatomic repulsions are also very important and can overwhelm the above coulombic attraction effects. That is, the density and polarizability effects may interfere constructively or destructively and it is not possible to predict the exact magnitudes of the respective effects.⁴ In other words, neither the magnitude nor the sign of the photoelastic coefficient can be predicted and no specific enhancing molecular properties can be identified.

Acoustic Velocities

The majority of work reported on acoustic velocities in polymeric materials has involved MHz frequencies. However, a number of GHz studies have also been published. A brief compilation of reported longitudinal acoustic velocities is given in Table 2.

The measured acoustic velocities in polymeric materials fall between those of metals (3000-6000 m/s) and liquids (900-1500 m/s)¹³ and it has been qualitatively determined that, over

Table 1: Photoelastic Coefficients of Organic Materials

MATERIAL	FORM/SYMMETRY	WAVELENGTH (microns)	P _{MAX}	REFERENCE
C (diamond)	CUBIC	0.54-0.59	0.38	5
C ₂ H ₇ NO ₃ S	MONOCLINIC	0.59	0.36	5
(C ₂ H ₅ NO ₂) ₃	MONOCLINIC	0.63	0.20	5
Poly(styrene)	AMORPHOUS	0.63	0.30	42
Poly(methyl methacrylate)	AMORPHOUS	0.63	0.30	42
OMTS-toluene* HMDS-styrene	THIN FILM	0.63	0.30	35

* OMTS = Octamethyltrisiloxane; HMDS = Hexamethyldisiloxane; thin films prepared by polymerization in a glow-discharge plasma with the indicated aromatic starting materials. The photoelastic constant that was reported is not a measured quantity; it is an estimate.

Table 2: Acoustic Velocities in Some Common Organic Materials
at Room Temperature

MATERIAL*	DENSITY (g/cm ³)	LONGITUDINAL VELOCITY (10 ³ m/s)	FREQUENCY ν	REF
P4M1P	0.835	2.2	1.8 MHz	40
		2.2	5-12 GHz	19
PMMA	1.191	2.7	0.6 MHz	38
		2.7	1 MHz	41
		2.7	6-30 MHz	39
		2.7	10-90 MHz	17
		2.7	11 GHz	17
PVC	1.386	2.3	1 MHz	41
		2.3	10-90 MHz	17
		2.4	10 GHz	17
ABS	1.022	2.1	0.6 MHz	38
		2.0	1.8 MHz	40
Poly(styrene)	1.102	2.4	0.6 MHz	38
		2.3	1 MHz	41
		2.4	31 GHz	20
Poly(carbonate)	1.194	2.2	1 MHz	15
		2.2	1 MHz	41
		2.3	5 MHz	44
Poly(sulfone)	1.240	2.3	1 MHz	41
		2.3	5 MHz	44
Poly(ether sulfone)	1.373	2.2	5 MHz	44
OMTS-toluene HMDS-styrene	1.7-1.9	1.8-2.2	70 MHz	35
EPON 828-Z	1.202	2.7	1-3 MHz	43

* P4M1P = Poly(4-methyl-1-pentene); PMMA = Poly(methyl methacrylate); PVC = Poly(vinyl chloride); ABS = Poly(acrylonitrile butadiene styrene); OMTS = Octamethyltrisiloxane thin film; HMDS = Hexamethyldisiloxane thin film.

wide ranges, as frequency increases the acoustic velocity increases.¹³⁻¹⁵ However, a brief examination of Table 2 shows that for materials below their glass transition temperature, the acoustic velocity dispersion is small over the MHz to GHz frequency regimes.

Material properties that affect the acoustic velocity have been investigated in the lower frequency range (< GHz) and a strong correlation with the volume of the material has been established.¹³⁻¹⁵ This relationship arises because of the volume dependence of the intermolecular potential. For example, replacing hydrogen atoms with fluorine atoms has the effect of lowering the acoustic velocity since the larger fluorine atoms will decrease the intermolecular attraction and result in an increase in the material's volume. Using a more common physical property to describe this effect, as density increases, acoustic velocity will increase. This concept has been successfully extended to copolymer and composite systems.¹⁵

Experimental studies have also shown that increasing the rigidity of the mainchain backbone of the polymer by the inclusion of phenylene groups results in increased acoustic velocities.¹⁵ This is due to the restricted conformational changes that can occur. Thus, to minimize the acoustic velocity and thereby maximize the figure of merit (M_2), a low density, elastic material is desired.

Acoustic Attenuation

The acoustic attenuation of polymeric materials, which involves both absorption and scattering, has received a great deal of attention because of the potential use of these materials in sonar devices.¹³⁻¹⁵ The attenuation coefficient, α , is defined by

$$\alpha = (1/x) \log(A_0/A) \quad (6)$$

where x is the distance traversed and A_0 and A are the initial and final wave amplitudes, respectively. α is measured in nepers/centimeter but commonly found expressed in terms of dB/cm. Experimentally, it has been found that absorptions in polymeric materials are either linearly or quadratically dependent on frequency.¹³⁻¹⁵ Linearly dependent absorption is also known as hysteresis absorption and is expressed as $\alpha/\nu = \text{constant}$ (ν = frequency). Hysteresis absorption has been observed in the GHz frequency regime.¹⁵⁻¹⁷

The microscopic description of the absorption processes occurring at sub-GHz frequencies involves contributions from molecular separations (a volume or density dependence) and structural rearrangements.¹³⁻¹⁵ For acoustic frequencies in the GHz regime, only limited structural rearrangements can

contribute to absorption as most materials can be regarded as being in the glassy state. (The glassy state corresponds to a large tensile modulus for the material.) In such cases, the absorption mechanism can be viewed as amplitude losses through the excitation of librations and/or rotations of mainchain side groups and limited partial segmental motions and reorientations of the mainchain backbone.¹⁵⁻¹⁷

A limited number of results have been reported on the acoustic absorption of polymeric materials in the GHz regime. This is due, in part, to the experimental difficulties in making these types of measurements: because of the high frequencies involved, Brillouin scattering experiments (light scattering from thermal phonons) are required.¹⁷⁻²⁴ Table 3 lists the reported attenuation coefficients of several polymeric materials measured at a number of acoustic frequencies.

The theoretical explanation for acoustic absorption and the results of experimental measurements (Table 3), indicate that highly crosslinked or crystalline type polymers are best at minimizing acoustic absorption. Note that this is the exact opposite of the type of material properties desired for a high figure of merit (M_2). As is so often the case in materials science, a compromise between competing material parameters must be reached and depends on the specific nature of the device design and application.

Scattering of acoustic waves is exactly like scattering of light waves; it depends on the size of the inhomogeneity. Therefore, choosing an acceptable optical material should go a long way to insuring an acceptable acoustic material.

Organic Acousto-Optic Material Evaluation

In evaluating organic materials for possible use in acousto-optic devices, the first issue to be considered is one of optical transparency. Polymeric materials can have excellent optical properties in the visible and near infrared spectral regions but will be absorbing in the infrared due to their chemical composition. This is an inescapable feature of organic materials, but one that can be mitigated by the use of unique molecular designs such as fluoridation and also by the use of thin films. The optical properties of polymers are well documented.^{11,15} For the purposes of this evaluation, only materials that are transparent in the visible spectral region will be considered.

Table 4 is a listing of several optically transparent polymeric materials and their important acousto-optic parameters. The density and refractive index entries are representative literature values.^{11,15,25} The table entries for the acoustic parameters are either the reported GHz values found in Tables 2 and 3 or have been estimated as discussed

Table 3: Acoustic Attenuation Factors for Some Common Organic Materials at Room Temperature

MATERIALS*	α LONGITUDINAL ATTENUATION (dB/cm)	FREQUENCY ν	α/ν ** (dB-s/cm) (10^{-7})	REF
P4M1P	1.4	2 MHz	7.0	15
	1.4	1.8 MHz	7.8	40
PMMA	1.4	2 MHz	7.0	15
	1.8	2.2 MHz	8.1	16
	3.7	5.5 MHz	6.7	16
	5.0	6 MHz	8.3	39
	7.7	10 MHz	7.7	39
	12.7	18 MHz	7.1	39
	12.6	20 MHz	6.3	39
	19.6	30 MHz	6.5	39
	2.1×10^4	11.3 GHz	18.5	17
PVC	5.7	1.5 MHz	37.8	17
	11.3	5 MHz	23	47
	16.1	10 MHz	16	47
	3.4×10^4	10.2 GHz	33.3	17
ABS	1.8	2 MHz	9.0	40
Poly(styrene)	0.4	0.5 MHz	8	45
	1.9	5 MHz	3.8	47
	3.8	10 MHz	3.8	47
	5.6	15 MHz	3.7	47
	5.8	20 MHz	2.9	47
Poly(carbonate)	21.7	5 MHz	43.4	44
	52.1	15 MHz	34.7	44
	86.9	25 MHz	34.7	44
Poly(sulfone)	8.7	5 MHz	17.4	44
	21.7	15 MHz	14.4	44
	34.7	25 MHz	13.9	44
	60.8	35 MHz	17.4	44
Poly(ether sulfone)	8.7	5 MHz	17.4	44
	26.0	15 MHz	17.3	44
	52.1	25 MHz	20.8	44
	65.0	35 MHz	18.6	44
Poly(ethylene)	3.3	2 MHz	16.5	15
	20	10 MHz	20	16

Table 3: Acoustic Attenuation Factors for Some Common Organic Materials at Room Temperature (cont.)

MATERIALS*	α LONGITUDINAL ATTENUATION (dB/cm)	FREQUENCY ν	α/ν ** (dB-s/cm) (10^{-7})	REF
OMTS-toluene				
HDTIS-styrene	0.4	70 MHz	0.06	35
EPON 828-Z	4.1	1 MHz	41.0	43
(EPOXY)	7.1	2 MHz	35.5	43
	10.5	3 MHz	35.0	43

* P4M1P = Poly(4-methyl-1-pentene); PMMA = Poly(methyl methacrylate); PVC = Poly(vinyl chloride); ABS = Poly(acrylonitrile butadiene styrene); OMTS = Octamethyltrisiloxane thin film; HMDS = Hexamethyldisiloxane thin film.

** Calculated using table entries.

Table 4: Acousto-optic Parameters for Some Common Transparent Organic Materials at Room Temperature.

MATERIAL [‡]	n	ρ (g/cm ³)	v_L (m/Sec)	p	M_1^* $\left(\frac{\text{cm}^2 \text{ sec/g}}{\times 10^{-7}}\right)$	M_2^* $\left(\frac{\text{sec}^3/\text{g}}{\times 10^{-16}}\right)$	M_3^* $\left(\frac{\text{cm sec}^2/\text{g}}{\times 10^{-12}}\right)$	α (10 ³ dB/cm) (1 GHz)
PMMA	1.49	1.191	2.7	0.3*	45.6	42.0	16.9	2.1
PC	1.60	1.194	2.3	0.3	88.0	26.6	38.2	3.5*
POLY(STYRENE)	1.60	1.102	2.4	0.3	91.3	99.2	38.0	0.30*
OMTS/HMDS	1.50	1.8	2.2	0.3	38.8	53.5	17.7	0.06*

[‡]PMMA = Poly(methyl methacrylate); PC = poly(carbonate); OMTS = Octamethyltrisiloxane thin film; HMDS = Hexamethyldisiloxane thin film.

*Indicates a calculated or estimated value. See text for a complete explanation.

below. The dispersion of acoustic velocities between MHz and GHz frequency regimes has been experimentally shown to be very small¹⁷ (see Table 2) and therefore, in the absence of a reported GHz value, the highest MHz value is used. With regard to acoustic attenuation, table values are calculated assuming hysteresis absorption using the constants found in Table 3. Based on the results reported for PMMA and PVC,¹⁷ such values are certainly correct to within an order of magnitude. Unfortunately, only a very limited number of photoelastic coefficients have been reported for polymeric materials and no clear method for estimating such values is available. Reported values (Table 1) are used where appropriate and an assumed value of 0.30 is used in the remaining cases. The assumed value choice is based on the observation that although the materials in Table 1 are widely different, p , the photoelastic coefficient, is essentially constant.

The figures of merit listed in Table 4 are calculated based on the corresponding table entries.

Figure 2 is a plot of the figure of merit, M_2 , versus attenuation, for a variety of inorganic materials and those in Table 4. From this plot we see that polymeric materials, although having a high figure of merit, also possess a very large acoustic attenuation in comparison to inorganic crystals. That is, present organic materials cannot compete with current inorganic materials.

Although the potential for polymeric materials looks bleak, new materials with novel properties are constantly being developed. One area that has yielded unique materials is the study and development of materials having large nonlinear optical properties.²⁶ Several materials with large delocalized π electron systems have been synthesized. Such materials have large polarizabilities and therefore may yield enhanced acousto-optic properties. One group of these nonlinear optical polymers, known as rigid-rod or ladder polymers, is especially interesting. These polymers (Fig. 3) are composed of interlocking phenylene rings with a limited number of side groups; features which should lead to reduced acoustic attenuation but relatively high acoustic velocity. Coupling the reduced attenuation with the increased polarizability (the π electron conjugation) suggests that these materials may have interesting acousto-optic potential. Unfortunately, little more can be said due to the lack of a means for estimating the photoelastic coefficient: material properties need to be measured.

With regard to other types of polymeric materials such as liquid crystals, acousto-optic measurements have been reported but involve complex effects due to shear induced structural reorientations (transverse wave effects).²⁷⁻³³

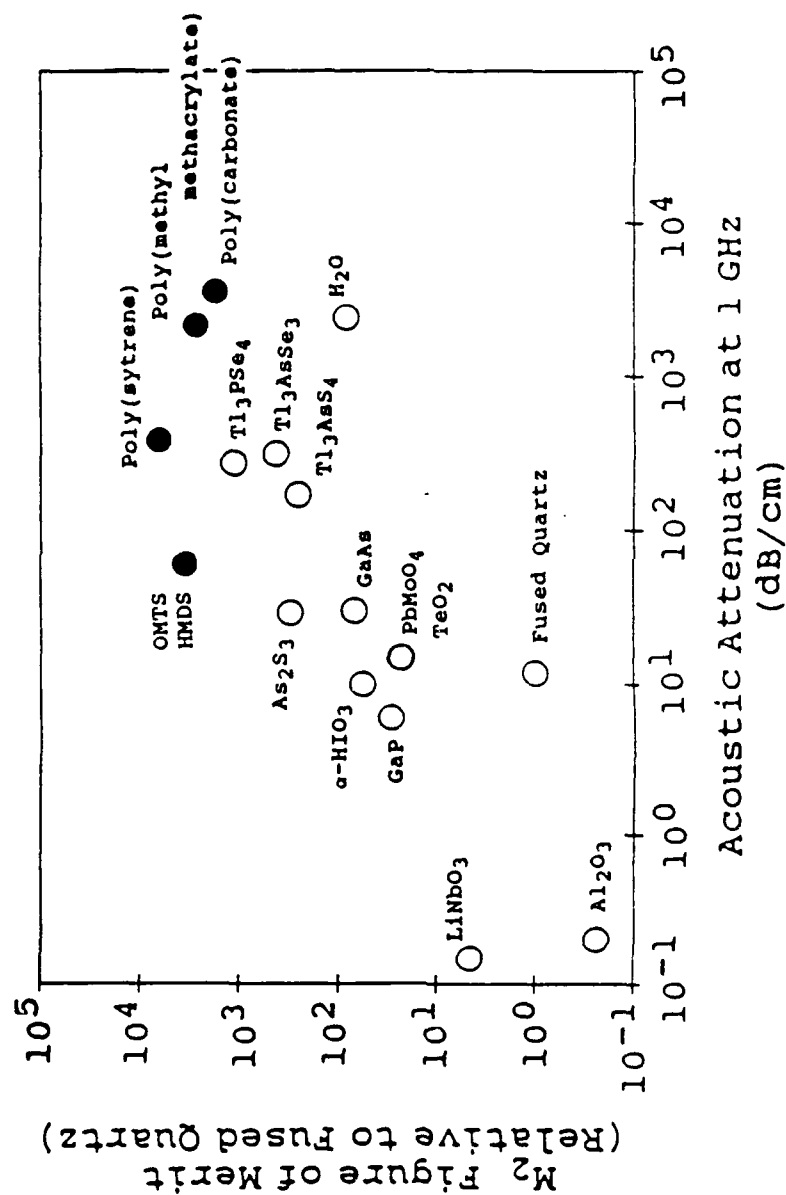


Figure 2: A plot of the acoustic attenuation (at 1 GHz) versus the figure of merit M_2 (relative to fused quartz) for a number of inorganic materials (open circles) and the polymeric materials given in Table 4 (filled circles). The inorganic data was obtained, and this figure was adapted, from Ref. 5.

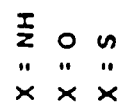
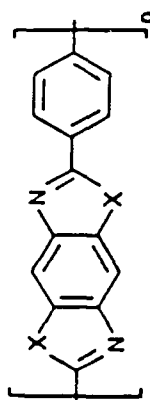
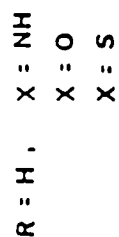
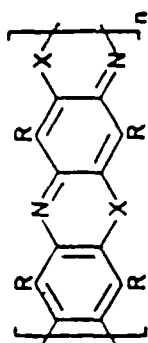
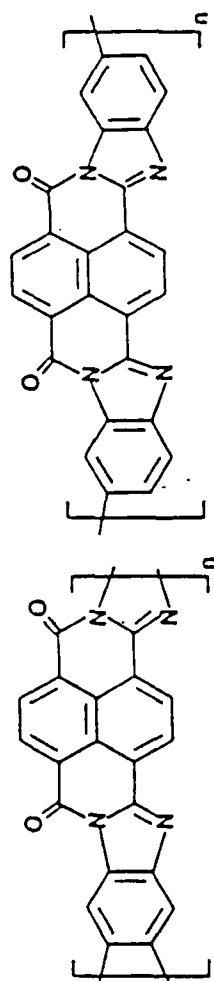


Figure 3: Examples of typical ladder polymers are diagrammed. The interlocking phenylene rings and the limited number of side groups may lead to reduced acoustic attenuation as compared to other polymer systems.

Finally, polymeric materials are finding increased use in surface acoustic wave (SAW) devices as thin films.^{34,35} SAW concepts^{36,37} may prove useful in a variety of applications and should be investigated. However, that is beyond the scope of this work.

LINEAR ELECTRO-OPTIC MATERIALS AND DEVICES

The application of an electric field (E) induces a change in the polarization (P) of all materials and can be described by the following tensor equation.⁴⁸ (The tensor coefficient subscripts are understood.)

$$P = P_0 + \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + \dots \quad (7)$$

P_0 is the material's intrinsic polarization and the χ 's are known as the material susceptibilities. The first term, $\chi^{(1)}$ is used to describe usual linear optical phenomena such as absorption, reflection and refraction. The latter two terms, $\chi^{(2)}$ and $\chi^{(3)}$, are known as the second-order and third-order susceptibilities, respectively, and are used to describe nonlinear optical effects such as the electro-optic effect and third harmonic generation.

Another notation for describing the effect of an electric field (E) on the optical properties of a material makes use of the index of refraction (n) directly.^{1,4}

$$(1/n^2) = (1/n_0^2) + r \cdot E + h \cdot EE + \dots \quad (8)$$

n_0 is the index of refraction at zero field and r and h are known as the linear and quadratic electro-optic coefficients. This type of notation is popular for describing effects in inorganic crystals.

The linear electro-optic effect, also known as the Pockels effect, is characterized by the second-order hyperpolarizability, $\chi^{(2)}$, or the linear electro-optic coefficient, r, and is only possible in noncentrosymmetric materials, i.e., materials which do not have centers of inversion. This also happens to be the symmetry requirement for the linear piezoelectric effect.^{1,4,5} (The piezoelectric effect is the production of an electric field in a material by the application of a stress or strain.) The majority of work conducted on linear electro-optic materials has focussed on inorganic crystals.^{1,4} However, organic/polymeric materials have been receiving increased attention because of the potential for large electro-optic effects coupled with better mechanical processing and design flexibility. Below, a brief description of the important molecular and material properties for enhanced electro-optic effects in organic materials is

presented. This is followed by a review of recent research efforts in material development with respect to applications at high modulation frequencies.

Organic Material Development

To achieve response times on the order of GHz, the optical processes occurring in solid materials must be mainly electronic in nature, i.e., vibrational and rotational motions are too slow. Thus, from a molecular point of view, enhanced electro-optic effects will be demonstrated by noncentrosymmetric molecules with easily polarized molecular electric fields. This latter condition is readily met in unsaturated organic molecules with highly conjugated π electron systems. The addition of substituent groups that induce a charge asymmetry, i.e., strong electron donor and acceptor groups, will also greatly enhance the electro-optic effect by making it easier to polarize such molecules. Great success has been achieved in synthesizing molecules of this type (second-order nonlinear optical molecules) using the above criteria.⁴⁹⁻⁵³

The incorporation of the active species into a macroscopic sample is also an area of current research; noncentrosymmetry with respect to molecular orientation must be maintained in order to observe electro-optic effects. Additionally, the more ordered the material, the greater the electro-optic effect. The two most popular and successful methods for ordering molecules in materials are electric field poling and Langmuir-Blodgett film deposition. Detailed descriptions of both of these ordering methods can be found elsewhere.⁵⁴⁻⁵⁷

Most of the recent research involving second-order organic materials for use in electro-optic devices has focussed on liquid crystal side chain polymers and guest/host type materials. Guest/host materials are prepared by dispersing the active molecules in a polymeric host material while liquid crystal side chain polymers are formed by attaching the active molecule to the polymer mainchain using spacer groups to decouple motion of the side chain from the backbone (See Fig. 4). In both cases, electric field poling is used to orient the material.

Comparison with Inorganic Materials

Table 5 contains several organic and inorganic electro-optic materials and parameters describing the magnitude of the reported electro-optic effect. The most common techniques for measuring these parameters are second harmonic generation ($\chi^{(2)}$) and modulated phase waveguiding (r). When comparing values, it is important to note that second harmonic generation can only arise from electronic contributions while electro-optic measurements can include contributions from molecular

LIQUID CRYSTAL SIDE CHAIN POLYMERS

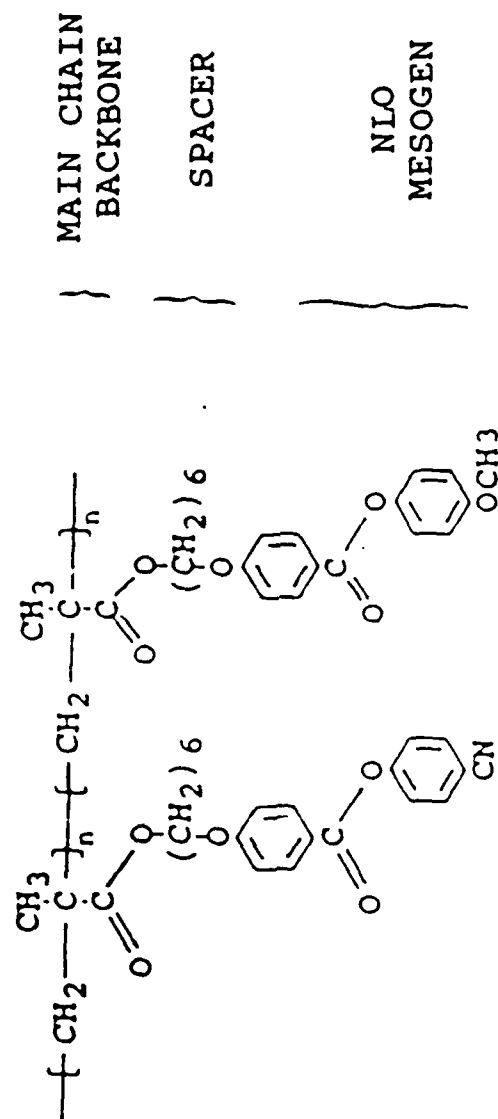


Figure 4: A schematic diagram of a liquid crystal side chain polymer.

Table 5: Linear Electro-Optical Materials

MATERIAL [†]	n	ε	χ ² (pm/V)	SHG r (pm/V)	λ (μm)	r (pm/V)	LEO λ (μm)	ν	REF
<u>ORGANIC CRYSTALS</u>									
MNA	2.0	4	500	60	1.064	67	0.63		58/66/68
UREA	1.48					1.9	0.63		68
POM	1.64					5.1	0.63		68
<u>POLYMERS</u>									
PNA/PMMA			0.9	0.45	1.064 0.63	0.5	0.63	MHz	65
MNA/PMMA			0.67	0.33	1.06 0.63	0.32	0.63	MHz	65
AZO DYE/PMMA	1.52	3.6			1.58	2.5	0.63	35kHz	55/69
HCC#1622			8.4	1.75	1.06 0.83				65
HCC#1238			36.5	10.0	1.34 0.83	20	0.83	10MHz	65

Table 5: Linear Electro-Optical Materials (cont.)

MATERIAL [†]	n	ε	χ^2 (pm/V)	SHG r (pm/V)	λ (μ m)	r (pm/V)	LEO λ (μ m)	ν	REF
HCC#1232			65.0	16.5	1.34 0.83				65
C22	1.6					14	0.83	250MHz	64
PC6S	1.7	3.3				2.8	0.83	1.8MHz	64

INORGANICS

LiNbO ₃	2.3 2.1	32	80	0.9		32 30.8	0.63 0.63		58 68
LiTaO ₃	2.2					30.3	0.63		68
GaAs	3.4					1.2	1.0		68
GaP	3.4					1.0	0.56		68
KDP	1.5	42	0.9	0.02		10.6			58

[†] MNA = 2-methyl-4-nitroaniline; POM = 3-methyl-4-nitropyridine-1-oxide; PNA = para-nitroaniline; PMMA = Poly(methyl methacrylate); HCC#, C22, PC6S = Hoechst/Celanese polymeric materials whose exact nature was not indicated.

vibrations and rotations.^{58,59} Therefore, an organic material with the same $\chi^{(2)}$ as an inorganic material (as measured by second harmonic generation) will probably have a smaller electro-optic coefficient (r), a consequence of the important contributions of lattice phonons to the electro-optic coefficient of inorganic crystals. In other words, the electro-optic effect in organic materials arises mainly from electronic contributions (polarizations of the loosely bound π electrons) while in inorganics the main contribution is from phonons (distortions of the nuclear framework and it's tightly bound electrons).⁶⁰⁻⁶²

The delocalized electronic nature of organic materials results in other material properties that are very important to electro-optic effects. One of the most important involves modulation frequency.^{55,57,58}

The response time of electro-optic devices depends on the dielectric properties of the material and favors lower values: the bandwidth per modulating power ($\Delta\nu/P$) of a guided-wave modulator is given by^{55,57}

$$\Delta\nu/P \propto [1/(1 + (\epsilon/\epsilon_0))] \quad (9)$$

while for a traveling wave modulator the rise time is described by^{55,57}

$$t_r \propto (\epsilon/\epsilon_0)^{1/2} - n \quad (10)$$

where ϵ is the static dielectric constant. The dielectric constants of organic materials are, in general, substantially lower than those of inorganic materials and are nondispersive.⁶³ The dielectric losses ($\tan \delta$) in organics are also generally low and nondispersive (See Table 6). Therefore, organic materials should allow higher modulation frequencies (than inorganics) for the same voltage (Fig. 5). This is a consequence of the "disassociation" of polarizable electrons from nuclei in organic materials.

Experimentally, a variety of device designs are used to measure the electro-optic properties of materials; the two most common are diagrammed on the following pages. MHz modulation of a variety of organic materials has been amply demonstrated using these types of devices.^{64,65} With regard to higher frequency modulation, phase modulation of a liquid crystal side chain polymer, in one arm of a Mach-Zender interferometer, at one GHz has been reported but not published.⁶⁴ A theoretical calculation has also been reported, but not published, that indicates polymeric materials could be modulated up to 20 GHz (See Fig. 8).⁶⁵

Table 6: Indices of Refraction, Dielectric Constant and Dielectric Loss Values
for Selected Organic Polymeric Materials

MATERIAL	INDEX OF REFRACTION	ϵ DIELECTRIC CONSTANT	TAN δ	FREQUENCY ν
Poly(propylene)	1.49	2.2-2.3	3×10^{-4} - 1×10^{-3}	60-100 MHz
Poly(tetrafluoro- ethylene)	1.38	1.21	2×10^{-4}	$60-10^9$ Hz
Poly(acrylonitrile)	1.52	4.2 5.5 6.5	0.033 0.85 0.113	MHz kHz 60 Hz
Poly(vinyl chloride)	1.54	3.5 3.4 3.3	0.11 0.08 0.06	60 Hz 1 kHz 10 kHz
Poly(methyl methacrylate)	1.49	3.6 3.0 2.6 2.6 2.5	0.062 0.055 0.014 0.007 0.10	50 Hz 1 kHz 1 MHz 30 GHz 138 GHz
Poly(styrene)	1.59	2.61 2.5	3×10^{-4} 15×10^{-4}	Flat to 1 GHz Flat to 1 GHz
Poly(oxyethyleneoxy-terephthaloyl) (poly(ethylene terephthalate))	1.57	3.3 3.25 3.0 2.8	0.0025 0.005 0.016 0.003	60 Hz 1 kHz 1 MHz 1 GHz

All the data presented in this table were obtained from Ref 63.

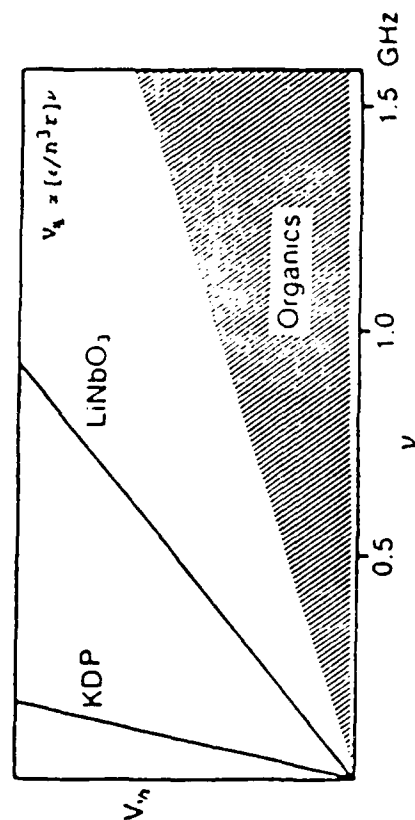


Figure 5: A comparison of inorganic and organic materials for a transverse electro-optic Pockels cell. Because of their lower dielectric constants, organic materials should permit higher modulation frequencies at equal voltages. This figure was adapted from Ref. 59.

POLYMERIC ELECTRO-OPTIC MODULATOR

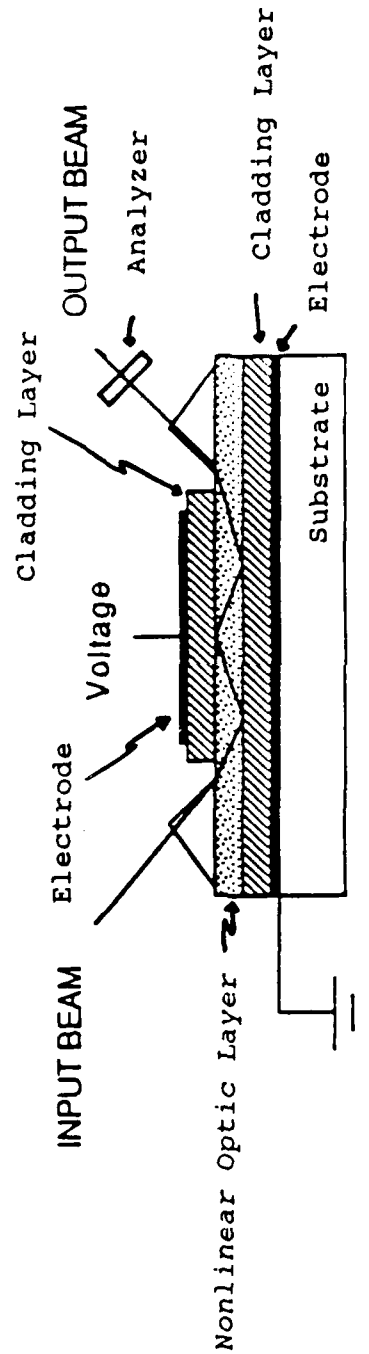


Figure 6: A schematic diagram of a polymeric electro-optic modulator. The nonlinear optically active film is poled prior to assembly of the device. The application of an electric field affects the light polarization which is detected using the analyzer (a polarizer).

TRAVELING-WAVE MODULATOR

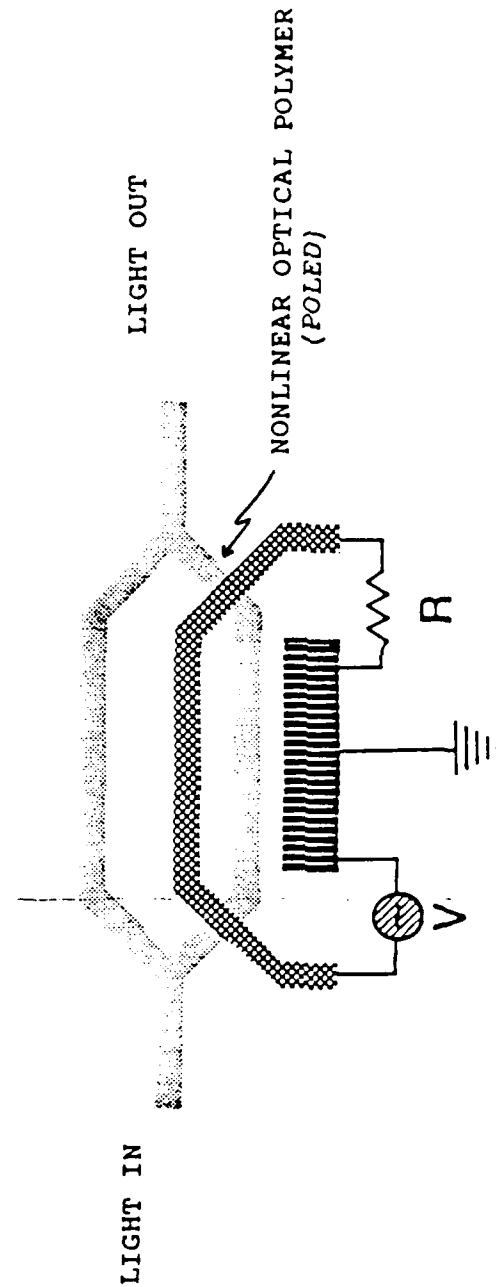


Figure 7: A schematic diagram of a traveling-wave waveguide. The input light is split into the arms of the waveguide and the electro-optic modulator produces a phase change in the light passing through one arm. The beams recombine to form the output. The intensity of the output wave depends on the induced phase shift. GHz modulation has been observed using this type of device (Ref. 64).

Traveling Wave E-O Modulator

Performance Predictions

LiNbO ₃ Modulator		NLO Polymer Modulator ¹
Maximum frequency	8 GHz	Limited by electrode loss only * (~ 20 GHz)
Active length	7.5 mm	15 mm
Overall length	4 cm.	4 to 5 cm.
Gap	6μm	6μm
Voltage	3.5V	< 5.1V
Power consumption	0.56W	< 0.51W
		$r \geq 20$ pm/volt

¹ Calculated by D. Haas

* Dielectric losses are less than LiNbO₃

Conductor losses are expected to dominate and to be lower for polymer designs

Figure 8: An analysis of the performance features of a traveling-wave electrooptic phase modulator. This information was presented at the Air Force Office of Scientific Research Nonlinear Optical Polymers Contractors Review, April, 1988, by J. Stamatoff of Hoechst/Celanese.

In conclusion, organic and polymeric materials have several advantages over inorganic materials for use in electro-optic devices: ease and flexibility in mechanical processing, high optical damage thresholds, low modulating voltages, low dielectric constants and large electro-optic coefficients. (The largest known electro-optic coefficient was measured for the organic crystal methylnitroaniline, 67 pm/V).^{66,67} GHz modulation in organic polymeric materials has been observed and research is underway to extend this to higher frequencies.

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